HUMAN EXPOSURE ASSESSMENT FOR METHAMIDOPHOS

HS-1825

By

W. Wendy Zhao, Staff Toxicologist Tareq A. Formoli, Associate Environmental Research Scientist

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California Environmental Protection Agency
Department of Pesticide Regulation
Worker Health and Safety Branch
1001 I Street
P.O. Box 4015
Sacramento, CA 95812-4015
www.cdpr.ca.gov

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HUMAN EXPOSURE ASSESSMENT FOR METHAMIDOPHOS

I. ABSTRACT

Methamidophos (O.S-dimethyl phosphoramidothioate) is a broad spectrum insecticide used in California on agricultural crops only. These agricultural uses are limited to potatoes, cotton and tomatoes. Methamidophos has no registered uses in residential settings. From 1998 through 2002, there were 14 illness/injury cases associated with exposure to methamidophos in combination with other pesticides, in California. As an anticholinesterase organophosphorus ester, methamidophos primarily affects plasma, red blood cell, and brain cholinesterase. Animal studies indicate that the majority of the dermally absorbed methamidophos would be excreted in the urine and a lower percentage would be converted to CO₂ and eliminated the by respiratory tract. The air monitoring studies indicated that non-occupational exposures to ambient/off-site levels of methamidophos will be minimal. We do not, therefore, intend to generate additional off-site exposure estimates at this time. The dermal absorption of methamidophos in humans was determined to be 29%. The acute absorbed daily dosage (acute ADD) for workers handling methamidophos is estimated to range from 20.0 µg/kg/day for a mixer/loader/applicator treating tomatoes or potatoes to 652.6 µg/kg/day for an aerial flagger for cotton. The acute ADD for fieldworkers is estimated to range from 0.83 µg/kg/day for a potato harvester (by hand) to 4.43 μg/kg/day for a tomato staker, tier, transplanter, or pruner. The seasonal average daily dosage (SADD) for handlers is estimated to range from 5.01 µg/kg/day for a mixer/loader/applicator treating tomatoes or potatoes to 163.16 µg/kg/day for an aerial flagger for cotton. The SADD for fieldworkers is estimated to range from 0.26 µg/kg/day for a cotton scout to 0.89 µg/kg/day for a tomato staker, tier, transplanter or pruner. The annual average daily dosage (AADD) for handlers is estimated to range from 1.67 µg/kg/day for a mixer/loader/applicator treating tomatoes or potatoes to 54.39 µg/kg/day for an aerial flagger for cotton. AADD for fieldworkers is estimated to range from 0.07 µg/kg/day for a cotton scout, a tomato staker, tier, transplanter or pruner to 0.21 µg/kg/day for a tomato scout or irrigator. The lifetime average daily dosage (LADD) for a handler is estimated to range from 0.89 µg/kg/day for a mixer/loader/applicator treating potatoes or tomatoes to 29.01 µg/kg/day for an aerial flagger for a cotton field application. LADD for fieldworkers is estimated to range from 0.03 µg/kg/day for a cotton scout to 0.11 µg/kg/day for a tomato scout or irrigator.

A risk characterization document for methamidophos is currently being prepared by the Department of Pesticide Regulation because animal studies showed that methamidophos could cause brain acetylcholinesterase inhibition and FOB (functional observation batteries) effects. This report was prepared as part of the Department's risk characterization document for methamidophos.

II. INTRODUCTION

Methamidophos (O,S-dimethyl phosphoramidothioate) is used as a broad spectrum agricultural organophosphate insecticide to control pests such as aphids, thrips, leafhoppers, whiteflies, beet armyworms, cabbage loopers, lygus bugs, mites, Colorado potato beetles, cutworms, and potato tuberworms. Methamidophos was first registered by Miles, Inc. with the United States Environmental Protection Agency (U.S. EPA) in 1972 under the trade name Monitor. As of October 2004, there are three products registered in California, by Bayer Corp., Bayer CropScience and Valent U.S.A. Corp. that contain methamidophos as the active ingredient (AI). Methamidophos is a federal and California restricted-use pesticide due to acute dermal toxicity and residue effects on avian species. Therefore, this pesticide is limited to use by or under the direct supervision of a certified applicator. It was listed as one of 200 priority chemicals to be reviewed under the Birth Defects Prevention Act of 1984.

Methamidophos is a Toxicity Category I pesticide and has the potential for worker exposure from agricultural uses. The human exposure assessment for methamidophos provides essential information for the risk assessment of this pesticide. This document will be an integral part of the risk characterization document (RCD). It will also serve as a basis for developing mitigation strategies if exposure to methamidophos is found to cause excessive risk.

III.FACTORS DEFINING EXPOSURE SCENARIOS

1. Physical and Chemical Properties

Physical and chemical properties of methamidophos, as mentioned below, were obtained from Mobay Chemical Corporation (Minor, 1980; Mayor and Barnett, 1985), the Merck Index (Budavari *et al.*, 1996), and the U.S. EPA (1999a).

Methamidophos (CAS Registry # 10265-92-6) is the common name for O,S-dimethyl phosphoramidothioate. Its empirical formula is C₂H₈NO₂PS. Methamidophos is a colorless to white crystalline solid with a strong mercaptan-like odor and a melting point of 46.1°C. Its molecular weight is 141.13. Methamidophos is readily soluble (> 200 g/L) in water, acetone, dimethylformamide, dichloromethane, and 2-propanol. It is also soluble in n-octanol at 50-100 g/L, toluene at 2-5 g/L, and n-hexane at <1 g/L. Methamidophos can be stored in a cool dry place but not below 15°F. It has a vapor pressure of 3 x 10⁻⁴ mmHg at 30°C. The octanol/water (1:1) partition coefficient for methamidophos is 0.22 at 20°C (Log K_{ow} is –0.66, Magee, 1982). The chemical structure of methamidophos is shown in Figure 1.

$$O$$
 $CH_3O \setminus ||$
 $P - NH_2$
 CH_3S

Figure 1. The Chemical Structure of Methamidophos.

2. U.S. EPA Status

In 1982, the U.S. EPA issued a registration standard based on its assessment of the available data on methamidophos and identified it as a restricted-use pesticide due to acute dermal toxicity and residue effects on avian species. In 1997, an agreement between the registrants (Bayer Corp. and Valent U.S.A. Corp.) and the U.S. EPA resulted in limiting the uses of methamidophos to potatoes and cotton and a FIFRA Section 24(c) use on tomatoes only, due to the Agency's concerns over illness incident reports (Fort, 1998). In addition to the use deletions, the registrants committed to require use of a closed system for mixing and loading by December 1999 (U.S. EPA, 2000a).

On October 11, 2002, the U.S. EPA published in the Federal Register a notice announcing the availability of the Interim Reregistration Eligibility Decision (IRED) document and technical support documents for methamidophos. EPA has determined that methamidophos is eligible for reregistration. Mitigation measures for methamidophos include a phase out of methamidophos use on cotton by 2007 due to the ecological toxicity concerns.

3. Formulations

To date, there are three methamidophos-containing products registered in California, Monitor[®] 4 Liquid Insecticide (Bayer Corp.), Monitor[®] 4 Spray (Valent U.S.A. Corp), and Monitor[®] 4 Liquid Insecticide (Bayer CropScience). The former two are emulsifiable concentrates with 40 percent AI by weight, containing 4 pounds (lbs) AI per gallon, and later one is aqueous concentrate with 40% AI.

4. Usage in California

Methamidophos is marketed in California under the trade name of Monitor[®]. Figure 2 summarizes methamidophos major uses in California for the most recent five years for which data are available (DPR, 1999, 2000a, 2000b, 2002, 2003).

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Figure 2. Methamidophos Applied to Various Commodities in California, 1998 - 2002.

In addition to the target crops (cotton, potatoes and tomatoes) on the product labels, methamidophos was also used on alfalfa, cole crops, sugarbeets and some other crops in these years. Although an agreement between the registrant and U.S. EPA in 1997 and 1998 limited its use to potatoes, cotton and tomatoes (U.S. EPA, 2000a), methamidophos in the channels of trade at the time of the agreement are allowed to be used. Overall, the amounts of methamidophos applied declined during these years (Fig. 3).

Methamidophos can be applied by groundboom or aerial application equipment to cotton, tomatoes and potatoes and by sprinkler irrigation (i.e., chemigation) to potatoes only. The highest rate of application is 1 lb AI/acre.

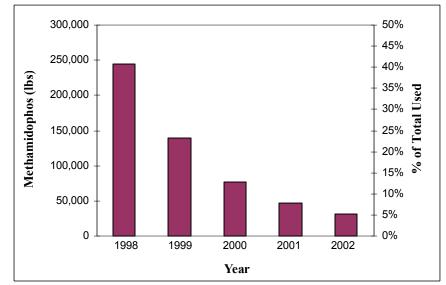


Figure 3. Total Methamidophos Applied In California, 1998 – 2002.

5. Label Precautions

All methamidophos products are Toxicity Category I with the signal word "Danger, Poison" for their acute toxicities. Methamidophos can be fatal if swallowed, inhaled or absorbed through skin. Hazards of ingestion, inhalation, and dermal or eye contact have been indicated on the product labels. Applicators and other handlers must wear the following protective clothing and equipment:

- Coveralls over short-sleeved shirt and short pants.
- Chemical-resistant gloves.
- Chemical-resistant footwear plus socks.
- Protective eyewear.
- Chemical-resistant headgear.
- Chemical-resistant apron when cleaning equipment, mixing or loading.
- A respirator with either an organic vapor-removing cartridge with a prefilter approved for pesticides (MSHA/NIOSH approval number prefix TC-23C), or a canister approved for pesticides (MSHA/NIOSH approval number prefix TC-14G).

6. California Requirements

Closed System for Mixing/Loading

Under California regulations, "Employers shall provide closed systems for employees who mix or load liquid pesticides in toxicity category one" (Title 3, California Code of Regulations [3 CCR] 6746(a)). Therefore, mixing and loading methamidophos must be conducted using closed systems in California, and handlers were assumed to mix/load using a closed system in this document.

Protective Clothing and Personal Protective Equipment

California regulations require eye protection and gloves be used for nearly all handling activities. Under California regulations, employees must wear protective eyewear when required by pesticide product labeling or when employees are engaged in mixing or loading and ground application (3 CCR 6738(b)(1)). Also, employees must wear gloves when required by the pesticide product labeling or when employees are engaged in mixing or loading (3 CCR 6738(c)(1)).

Mixer/loaders using a closed system and enclosed cabs are allowed by state regulation to substitute, usually less protective PPE, than listed on product labels. California regulations state (3 CCR 6738(i)(1)): "Persons using a closed system to handle pesticide products with the signal word 'DANGER' or 'WARNING' may substitute coveralls, chemical resistant gloves, and a chemical resistant apron for personal protective equipment required by pesticide product labeling." In addition (3 CCR 6738 (i)(5)), "Persons occupying an enclosed cab (including cockpit) may substitute work clothing for personal protective equipment required by pesticide

product labeling. If respiratory protection is required it must be worn, except in an enclosed cockpit".

Combining the PPE requirements from the product labels and California regulations, methamidophos applicators were assumed to wear coveralls, chemical-resistant gloves, chemical-resistant apron, shoes plus socks, and protective eyewear for this exposure assessment. For mixer/loaders, since the closed system is required, a respirator is not required.

7. Reentry Interval/Preharvest Interval

The label restricted entry interval (REI) is 48 hours. The label also indicates "each 48-hour REI is increased to 72 hours in outdoor areas where average rainfall is less than 25 inches a year". In California, 48-hour REI is increased to 3 days by regulation because average rainfall is less than 25 inches. "Whenever the pesticide product labeling specifies that a restricted entry interval be adjusted when outdoor applications are made in areas that receive less than 25 inches of average annual rainfall, the restricted entry interval specified for the dry areas shall apply to all outdoor applications in the State" (3 CCR 6774(e)).

The pre-harvest intervals (PHIs) vary depending on the product labels. The PHIs for tomatoes are listed as 7, 10, or 14 days on the different labels. One SLN label (CA-780163) indicates 7 days for fresh fruit and 14 days for processing. There is more exposure concern in fresh fruit (harvested by hand) than processing (harvested by machine). Also, 7 days is the shortest PHI. Therefore, with the most conservative estimation, 7 days was used as a PHI for the exposure assessment of tomato harvesters in this document. The cotton PHI is listed as 50 days on product labels. Any future changes in PHI will necessitate an evaluation and possible adjustment to harvester exposure estimate.

Methamidophos may be reapplied at intervals of 7 to 10 days as necessary but not more than 5 applications per crop season for tomatoes. The product labels do not provide a definite application interval for cotton, stating, "A second application may be needed for heavy infestations."

8. Reported Illnesses in California

The Pesticide Illness Surveillance Program database maintained by the Worker Health and Safety Branch (WHS) indicated that from 1998 through 2002, there were 23 reported illnesses/injuries associated with agricultural use of methamidophos (Mehler, 2004). All of these 23 cases were exposures to methamidophos used in combination with other pesticides, including dimethoate, mepiquat chloride, sulfur, and various adjuvants. Among these 23 cases, fifteen were systemic in nature (65% of total cases), eight with respiratory and systemic symptoms (35% of total cases), and one with skin and eye effects and systemic symptoms (4% of total cases). No deaths were associated with methamidophos exposure during this period. Table 1 summarizes the illnesses related to various agricultural work activities in California during 1998 to 2002. Except 2002, all of illness cases involved fieldworkers exposed to drift. All seventeen cases in 2002 were from a single episode due to a crash of an aerial applicator.

All affected people were emergency response personnel and construction workers. No field workers or residents were exposed as a result of this accident.

Table 1. Summary of Reported Illnesses Related to Agricultural Use of Methamidophos in California, 1998 - 2002 a.

Year	Illness Count ^b							
	Applicator	Mixer/Loader, Aerial	Flagger	Field Residue	Drift Exposure	Other Exposure	Sum	
1998	0	0	0	0	0	0	0	
1999	0	0	0	0	0	0	0	
2000	0	0	0	0	5	0	5	
2001	0	0	0	0	1	0	1	
2002	0	0	0	0	0	17	17	

^a Data from the illness report (Verder-Carlos, 2002).

9. Significant Exposure Scenarios

The U.S. EPA identified five major occupational handler exposure scenarios based on the types of equipment and techniques that can be used to apply methamidophos (U.S. EPA, 1999a). In addition to these scenarios, a mixing/loading/application scenario was considered for ground applications, since the same person often mixes, loads and applies. To make this exposure assessment clear, "mixing/loading of liquid formulation for aerial/chemigation application" as listed in the Reregistration Eligibility Decision document (RED, U.S. EPA, 1999a) was separated into "mixing/loading of liquid formulation for aerial application" and "mixing/loading of liquid formulation application" scenarios. Chemigation involves mixing/loading that includes application to the irrigation system. Therefore, there are seven scenarios addressed in this document:

- Mixing/loading of liquid formulation for aerial application;
- Mixing/loading of liquid formulation for chemigation application (potatoes only);
- Mixing/loading of liquid formulation for groundboom application;
- Mixing/loading/application of liquid formulation for groundboom application
- Application with a fixed-wing or a rotary aircraft;
- Application with groundboom equipment;
- Flagging for aerial spray applications.

In addition to handlers, reentry workers also have the potential for exposure to methamidophos. Based on cultural practices identified by U.S. EPA (1999a), this document identified six reentry worker exposure scenarios in California:

^b All illness cases are methamidophos used in combination with other pesticides.

- Cotton scouting;
- Scouting and irrigating tomatoes;
- Staking and tying tomatoes;
- Transplanting and pruning tomatoes;
- Harvesting tomatoes;
- Harvesting potatoes.

One of the scenarios assessed by U.S. EPA, early scouting for cotton, was omitted since late scouting should be protective of early scouting (crops grow higher and bigger, thus more frequent contact would happen between scouts and leaves treated with pesticide). Another scenario assessed by U.S. EPA, sorting and packing potatoes, was not considered significant, as the top part of the plant, where most of the pesticide residues are anticipated to be present, is discarded at harvest, and tubers are not treated before sorting and packing.

Cotton is mechanically harvested in California. The PHI for cotton is 50 days. No significant exposure is anticipated for the cotton harvest crews.

Under the Worker Protection Standard scouting is considered as a handler activity only during the period of an application, or during the REI listed on the product labeling. The exposure of scouts during the REI should be much less than other handler (mixer/loader and/or applicator) exposure. Therefore, exposure estimates for scouts should be adequately covered by those handler activities' exposure estimates. In this document, only the exposure of scouts who enter the treated field after REI will be estimated.

Residential exposures are not anticipated to be significant, as methamidophos has no registered uses in residential settings; all registered uses are agricultural.

IV. PHARMACOKINETICS

1. Dermal/Inhalation Absorption

1.1 Dermal Absorption

All dermal absorption studies were evaluated by Thongsinthusak (2000a,b,c) as briefly cited below:

Rat:

Chevron Environmental Health Center, Inc. conducted a dermal absorption study of methamidophos in male Sprague-Dawley® rats (Bagos and Beatty, 1991). The test material was administered on the dorsal trunk of rats. After dermal application of the test material, rats were placed individually in Metrap® restraining metabolism chambers for their respective exposure times. The appropriate methods were used to collect methamidophos and its metabolites from the various media. The estimated dermal absorption was calculated as percent of the applied dose found in the treated skin, blood, urine, feces, carcass, cage rinse, carbon dioxide trap and

volatile trap. The dose and estimated dermal absorption values were evaluated by WHS (Thongsinthusak, 2001a). However, this study was considered unacceptable because the total dose recoveries for several exposure times were very low (63.8% to 88.8%). The recovery from the 10-hour exposure period for the lowest dose (5 μg/cm²) was 63.8%, which is very low and unacceptable. This low dose is typically an exposure level experienced by agricultural workers. The low recovery was likely due to poor trapping efficiency of volatile ¹⁴CO₂ or other metabolites. Also, improper handling and analysis of the samples could have resulted in low recovery. Additionally, the doses of methamidophos employed in this study were not mixed with a formulation blank, i.e., other ingredients in the commercial formulation of methamidophos minus the active ingredient (Thongsinthusak, 2001a).

Monkey:

Sierra Biomedical, Incorporated conducted a dermal absorption study of methamidophos in four male rhesus monkeys (Fuller, 2000). [¹⁴CH₃S]-Methamidophos was prepared in 0.9% saline for IV dosing and [¹⁴CH₃S]-Tamaron 600 SL for dermal dose administration. Prior to the dermal or intravenous administration, the animals were placed in restraint chairs and were kept in the chairs for 8 hours following dosing. The animals were then transferred to metabolism cages. Blood, urine, feces and other samples were collected at various time points after the IV and dermal dosing.

For IV dosing, an average of 11.35% of the administered dose was recovered in the urine and 0.51% was recovered in the feces. For dermal administration, the majority of the applied dose (57.3%) was recovered in the skin swabs with soap and water. Alcohol swabs contained 4.10% and tape strips contained 0.15% of the administered dose. Other dose recoveries were: Duoderm® patch 2.76%, dermal dome 1.33% and feed biscuits 0.11%. The mean dose was approximately $10~\mu\text{g/cm}^2$. The mean total recovery of unabsorbed dose was 65.75%. The dermal absorption of methamidophos was calculated to be 11.3% (Thongsinthusak, 2001b). This dermal absorption is not acceptable because the mean recovery following the IV administration was very low (11.35% in the urine and 0.51% from the feces as mentioned above), indicating the loss due to volatile metabolites.

Human:

A dermal absorption study of methamidophos in six healthy male volunteers was conducted by Pharma Bio-Research Clinics, B.V of The Netherlands (clinical phase) and XenoBiotic Laboratories, Inc. of the United States (analytical phase) (Bayer Corp., 2000). The six volunteers were administered a single 100-μL dose of [14CH₃S]-methamidophos in the Tamaron 600 SL formulation. The mean dose of 71 μg of radiolabeled methamidophos was applied topically to an area of 24 cm², equivalent approximately to 3 μg AI/cm². All samples (urine, blood, feces, swabs, skin rinses, tape strips, the dome, template and gauze) at various time points were processed accordingly and analyzed for radioactivity, using a Beckman liquid scintillation spectrometer. The average recoveries of radioactivity as percent of applied dose were 70.54% (swab, skin rinsate, dome, Duoderm® patch, and gauze pads), 0.89% (tape stripping), 0.0% (feces), and 0.55% (urine). The total average recovery was 71.98%. The dermal absorption of methamidophos was calculated to be 6.4% (Thongsinthusak, 2001c). However, the average recovery of unabsorbed dose in the dermal absorption study in humans was 70.54%. That means

approximately 29% of the administered dermal dose could have been absorbed (indirect estimate). This dermal absorption value represents an extreme case scenario, and this conservative dermal absorption value of 29% was used in the exposure calculations.

In a dermal absorption study, it is essential that a compound be radiolabeled at a position at the core of the molecule in order to prevent loss of metabolite(s) due to volatilization. A new dermal absorption study using ³²P-methamidophos in animals is recommended by the Department of Pesticide Regulation (DPR) (Thongsinthusak, 2001c).

1.2 Inhalation Absorption

No inhalation absorption studies are available for methamidophos. In the absence of these data, a default inhalation absorption rate of 100% was assumed. This default value was used in this document for calculations of doses absorbed via inhalation.

2. Animal Metabolism

In rats, methamidophos was extensively absorbed and initially eliminated relatively rapidly followed by the second slow phase (Cavalli, 1969). Each animal was orally administered the compound labeled with either ¹⁴C or with ³²P. In the ¹⁴C study, it was found that at least 60% of the applied dose was either eliminated and/or decomposed in the first 24 hours following the feeding. The greatest portion of the radioactivity in the ¹⁴C study was excreted either through urine or as ¹⁴C-CO₂ via the respiratory system. The feces contained very little radioactivity (< 5%). In the ³²P experiment, the majority of radioactivity (approximately 70%) was eliminated in the urine. The feces contained very little radioactivity (less than 5%). The radioactivity remaining in the dosed animals after the initial rapid excretion was evenly distributed throughout the body. The elimination of the residual radioactivity from the body was the second or slow phase of excretion. Based on the identity of the detected radioactive metabolites isolated from the urine, feces and tissues, the degradation of methamidophos is hydrolytic in nature.

The proposed metabolic pathway of methamidophos in rats is shown in Figure 4. The degradation appears to take place first with a rupture of the P-N bond to form O,S-dimethyl phosphorothioate (II) plus ammonia. Demethylation takes place first at the P-S bond and then at the P-O bond to form, in order, methyl dihydrogen phosphate (III) then phosphoric acid (IV). These metabolites (II, III, and IV) are not considered toxic.

CH₃O
$$\stackrel{O}{\underset{P-NH_2}{\text{II}}}$$
 $\stackrel{CH_3O}{\underset{P-OH+NH_3}{\text{CH}_3S}}$ $\stackrel{O}{\underset{P-OH+NH_3}{\text{CH}_3O}}$ $\stackrel{O}{\underset{P-OH}{\text{CH}_3O}}$ $\stackrel{O}{\underset{P-OH}{\text{III}}}$ $\stackrel{II}{\underset{P-OH}{\text{III}}}$ $\stackrel{IV}{\underset{P-OH+NH_3}{\text{IV}}}$ (methyl dihydrogen phosphate) (phosphoric acid)

Figure 4. Proposed Metabolic Pathway of Methamidophos in Rats (Crossley and Tutass, 1969).

Mahajna and Casida (1998) examined *N*-hydroxylation as an alternative to the controversial *S*-oxidation proposed earlier for methamidophos activation as shown in Figure 5:

$$CH_{3}O \bigvee_{P \text{ - NH}_{2}}^{O} P \text{ - NH}_{2}$$

$$CH_{3}O \bigvee_{P \text{ - NH}_{2}}^{O} P \text{ - NH}_{2}$$

$$CH_{3}O \bigvee_{P \text{ - NH}_{2}}^{O} CH_{3}O \bigvee_{P \text{ - NHOH}}^{O} CH_{3}S$$

$$N-\text{hydroxymethamidophos}$$

Figure 5. Candidate Mechanisms for Bioactivation of Methamidophos by S-and N-Oxidation (Mahajna and Casida, 1998).

N-Hydroxymethamidophos is less potent than methamidophos as an acetylcholinesterase inhibitor and toxicant possibly associated with its rapid hydrolysis.

3. Dermal Sensitization and Eye Irritation

Methamidophos is readily absorbed by the intact skin of mammals. The compound does not elicit a dermal sensitization response in humans or rabbits according to studies by Porter *et al.* (1987) and Hixson (1980). Hixson (1980) reported methamidophos-induced eye irritation in rabbits.

V. ENVIRONMENTAL CONCENTRATIONS

1. Air

Methamidophos air monitoring studies, one ambient and one off-site, were conducted in California in 2002.

The California Air Resources Board (ARB) conducted the first study in Fresno County from July 8 through August 23, 2002 (ARB, 2003a). California growers primarily use acephate and methamidophos to control a variety of plant and soil insects. Five ambient air sampling sites were selected in relatively high-population areas or in areas frequented by people (e.g., schools

or school district offices, fire stations, or other public buildings). Background samples were collected at the ARB's regular air monitoring site in Fresno. At each site, 28 discrete 24-hour samples were collected, Monday through Friday (4 samples/week), during the 7-week sampling period. Collocated (replicate) samples were collected for seven dates (each Wednesday) at each sampling location. Of the 168 ambient samples collected, 10 contained concentrations of methamidophos above the limit of quantification (LOQ, the original study referred it as the estimated quantitation limit, EQL) of 3.5 ng/m³, 7 were found to have results equal to or above the limit of detection (LOD, the original study referred it as method detection limit, MDL), but below the reported LOQ, were reported as "detected" and 151 were below the LOD. Daily concentrations of methamidophos ranged from < LOD to 16 ng/m³ (2.8 parts per trillion by volume (pptv)). The highest concentration was measured at the San Joaquin Elementary School (SJS) site. Seven-week average concentrations ranged from 0.55 ng/m³ (0.095 pptv) to 1.4 ng/m³ (0.24 pptv).

The ARB conducted the off-site monitoring study in San Joaquin County from September 2 through September 3, 2002 (ARB, 2003b). Chlorothalonil and methamidophos were applied to a tomato field. Before the application, background air concentrations of methamidophos were monitored for approximately 23.3 hours. During the application, sample tubes were set to collect air samples for approximately 2.7 hours. After the application, air samples were sequentially collected in seven sampling periods. The approximate times for these sampling periods were 1.1, 2, 2.8, 13.4, 10.8, 13.1, and 23.6 hours for a total of about three days (approx. 66.8 hours) post application. Nine samplers were positioned around the field, one on each side, one in each corner and one collocated on the down wind side. Ranges of methamidophos air concentrations are shown below:

Sampling Period	Approx. # Hours	Range of Methamidophos (ng/m ³)
Background	23.3	< LOD and NA
1	2.7	$<$ LOD $\sim 8.0E+02$
2	1.1	$<$ LOD $\sim 8.9E+02$
3	2.0	$<$ LOD $\sim 7.1E+02$
4	2.8	$<$ LOD $\sim 3.5E+02$
5	13.4	$<$ LOD $\sim 2.4E+02$
6	10.8	$<$ LOD $\sim 3.2E+01$
7	13.1	INVALID and 2.7E+01
8	23.6	< LOD ~ 2.7E+01

LOD = 3.0 ng/sample NA = Not Applicable

Of the 72 application samples collected, 34 of the 59 valid sample results for methamidophos were above the LOQ (15 ng/sample), 22 were below the LOD (3.0 ng/sample), 3 were above the LOD but below the LOQ and 13 samples were invalidated due to sampling problems. The highest concentration of methamidophos, 890 ng/m³ (150 pptv), also occurred at the East sampling site but during the second sampling period (one hour sample post application). Results of all background samples collected for methamidophos were < LOD.

Results from ambient and off-site air monitoring studies showed that air concentrations of methamidophos were extremely low. In the ambient air monitoring study, 90% samples contained methamidophos below the LOD of 0.86 ng/m³. On the basis of these studies, it is assumed that non-occupational exposures to ambient/off-site levels of methamidophos will be minimal.

2. Water

The hydrolysis of methamidophos was found to be related to temperature and pH (Leary, 1968; Magee, 1966). In solutions with a pH below 2, the half-life was a matter of hours. At pH 9, the half-life was 2.6 days at 25°C and 1.5 days at 37°C. In mildly acidic or neutral solutions, methamidophos showed remarkable stability at temperatures up to 80°C (less than 5% hydrolysis in 25 hours). The P-NH₂ bond is broken first, followed by hydrolysis of the CH₃SP grouping.

3. Soil

Methamidophos degrades at a relatively fast rate in soils. In laboratory experiments, Leary and Tutass (1968) found half-lives of 1.9 days in silt soil, 4.8 days in loam soil and 6.1 days in sandy soil. Sterilization of silt soil by autoclaving resulted in a considerable increase in the half-life, to about 6 weeks.

In laboratory experiments conducted by Horler *et al.* (1975), methamidophos was also found to undergo rapid degradation. In basic soils (pH 7.40 and 7.75), only 3 – 7% of the original activity was found after 4 days; in an acid soil (pH 4.30), 25% was present after 9 days. In the soils, there were differences in the degradation of metabolites. In clay-loam soils (pH 7.40), the metabolites degraded at a slower rate than in loam soils (pH 7.75). Since both soils had a similar pH, such differences may be connected with the fact that microorganisms play a role in the decomposition.

4. Dislodgeable Foliar Residue (DFR)

The term DFR is defined as the amount of pesticide residues that can be removed from both sides of the foliage surface using an aqueous surfactant. Generally, the leaf disc samples were rinsed and dislodgeable residues were analyzed by gas-liquid chromatography. The DFR is reported as the residues per leaf area (μ g/cm²). A general equation for calculating DFR and half-life (t ½) at a given time is:

$$DFR_t = DFR_0 \times exp(-kt)$$

In the above formula, DFR_0 represents initial DFR level, t represents the day after treatment, and t is the constant derived from regression. In the subsequent discussions, the data were analyzed by completing an exponential regression and the first-order rate kinetics calculation of the half-life. Post-application DFR studies were conducted following methamidophos use on cotton, tomatoes and potatoes and the results are shown in Table 2. DFR values used in exposure estimates were back calculated from equations generated from study data (Andrews, 2000).

4.1 Cotton

A DFR study of methamidophos following application to cotton was performed by Fujie (1986). The test was conducted in Fresno, California. The test was initiated on August 19, 1985 and completed on September 2, 1985. Monitor® 4S was applied at a rate of 1.0 lb AI/acre. Following the second application, samples were taken at 1 and 8 hours, then at 1, 2, 3, 4, 7 days. Three composite samples from the treated area and one composite sample from an untreated area were taken at each sampling interval. Each composite sample contained 48 one-inch leaf discs. These data were analyzed by conducting an exponential regression and the first-order rate kinetics calculation of half-life as shown in Table 2.

4.2 Tomatoes

Two studies, performed in California, measured methamidophos DFR following applications to tomatoes. The first study was conducted by Maddy *et al.* (1985) at San Diego, California. The application rate was 1.0 lb AI/acre. The replicated samples were taken from each of 25 plants each day. The first sample was taken approximately 24 hours after the application, then again every 24 hours, for a total of seven sampling days. DFR values reported ranged from 0.002 $\mu g/cm^2$ to 0.013 $\mu g/cm^2$. These values were significantly lower than those reported in the RED. Since the values were outside of the expected range and insufficient information was provided for validation, these data were not used in this assessment.

The second study was reported to U.S. EPA, the data were available in the RED (U.S. EPA, 1999a, MRID 44685501). The study was conducted in three areas: Fresno, California; Vero Beach, Florida and Tifton, Georgia. In this document, only the California data were used for estimating exposures of fieldworkers in the state. Field studies were conducted from late June to late August of 1995. Monitor® 4 was applied at the maximum label rate of 1.0 lb Al/acre 5 times at 7-day intervals. In each location, three replicate DFR samples and one blank sample were collected at the following intervals: prior to each treatment, immediately after the spray had dried (approximately 2 hours post-application), and 1, 2, 3, 5 and 7 days after each application (Table 2). Samples were also collected at 9, 11, 14, 21, 28 and 35 days after the final (fifth) application in each location. Mean field recoveries were between 70% – 120%.

4.3 Potatoes

Since no potato DFR data for California were available, potato DFR data from Stilwell, Kansas reported to U.S. EPA and used in the RED (U.S. EPA, 1999a, MRID 44685502) were used in this document. The field studies were conducted from June and July of 1996. Four applications of Monitor[®] 4 were performed at the maximum label rate of 1.0 lb AI/acre at 7-day intervals. DFR samples were collected as soon as sprays dried (i.e., at about 2 hours) and 1, 2, 3, 5, and 7 days after the first three applications, and for the fourth application, additional samples were collected at 9, 11, and 14 days after the application (Table 2). Most of the recovery values exceeded 80 percent, with the exception of two that were from the highest fortification level.

Table 2. Dislodgeable Foliar Residues (DFR) on Selected Crops Treated with Methamidophos ^a.

DAT ^b	DFR Value		Equation of	\mathbb{R}^2	Half-life		Site
	Observed	Calculated			(day)	Dates	
Cotton d			$DFR_t = 0.2815e^{-0.3665t}$	0.96	1.9	8/19/85 -	Fresno,
0	N/A e	0.2815				9/2/85	CA
1	0.17 ± 0.01	0.1951					
2	0.16 ± 0.03	0.1353					
3	0.08 ± 0.01	0.0938					
4	0.08 ± 0.004	0.0650					
5	N/A	0.0450					
6	N/A	0.0312					
7	0.02 ± 0.01	0.0216					
8	N/A	0.0150					
Tomatoes ^f			$DFR_t = 0.2646e^{-0.229t}$	0.73	3.0	6/95-	Fresno,
0	N/A	0.2646				8/95	CA
1	N/A	0.2104					
2	N/A	0.1673					
3	N/A	0.1331					
4	N/A	0.1058					
5	N/A	0.0842					
6	N/A	0.0669					
7	N/A	0.0532	0.21724				
Potatoes ^g			$DFR_t = 0.4838e^{-0.2173t}$	0.90	3.2	6/96-	Stilwell,
0	N/A	0.4839				7/96	KS
1	N/A	0.3894					
2	N/A	0.3133					
3	N/A	0.2520					
4	N/A	0.2028					
5	N/A	0.1632					
6	N/A	0.1313					
7	N/A	0.1056					
8	N/A	0.0850					
9	N/A	0.0684					
10	N/A	0.0550					
11	N/A	0.0443					
12	N/A	0.0356					
13 14	N/A N/A	0.0287					
		0.0231	ingredient/acre.				

The regression equations were determined by the authors of this document.

d Data based on study by Fujie (1986).

^e N/A: Not Available.

Data based on RED, MRID 44685501 (U.S. EPA, 1999a).
 Data based on RED, MRID 44685502 (U.S. EPA, 1999a).

VI. EXPOSURE ASSESSMENT

Methamidophos can be applied in California by air, chemigation, and groundboom application equipment. According to the U.S. EPA, the use of methamidophos is limited to cotton, potatoes, and tomatoes (U.S. EPA, 2000a). There is a potential for occupational exposure to ground and aerial crews handling methamidophos. Mixer/loaders, groundboom applicators, pilots, and flaggers may be exposed to methamidophos during handling. In addition, fieldworkers such as harvesters, irrigators, and cotton scouts entering previously treated areas can be exposed to methamidophos-treated foliage and surfaces. Non-occupational exposures (non-dietary) are not anticipated, as there are no residential or institutional uses of methamidophos in California.

Agriculture Use

1. Exposure of Handlers

There are no methamidophos-specific handler exposure data available in the DPR files. U.S. EPA has recently completed an exposure assessment as a part of the RED for methamidophos (U.S. EPA, 1999a). In the absence of any chemical-specific handler exposure data, U.S. EPA used the Pesticide Handlers Exposure Database (PHED, 1995), Version 1.1, to assess exposure to methamidophos handlers. PHED was developed by the U.S. EPA, Health Canada and the American Crop Protection Association to provide non-chemical-specific pesticide handler exposure estimates for specific handler scenarios. It combines exposure data from multiple field monitoring studies of different AIs. The user selects a subset of the data having the same or similar application method and formulation type as the target scenario. The use of non-chemical-specific exposure estimates is based on two assumptions (Versar, 1992): (1) that exposure is primarily a function of the pesticide application method/equipment and formulation type and not of the physical-chemical properties of the specific AI; and (2) that exposure is proportional to the amount of AI handled.

Although PHED provides the exposure data for various scenarios, PHED has limitations as a surrogate database. It combines measurements from diverse studies involving different protocols, analytical methods and residue detection limits. Most dermal exposure studies in the PHED use the patch dosimetry method of Durham and Wolfe (1962); residues on patches placed on different regions of the body are multiplied by the surface area of the region to estimate exposure to that region. The regions are then summed to provide a total body exposure estimate. Some studies observed exposure to only selected body regions such as the hands, arms and face, with the other body regions considered completely protected from exposure by work clothing. As a consequence, the estimate of dermal exposure for each body region is based on a different set of observations. Further, for some handler scenarios, the number of matching observations in the PHED is so small that they may not represent the target scenario well.

To increase the confidence in the estimate exposure data from surrogate study, WHS currently uses upper-bound estimates for acute exposure, so that WHS estimates the highest exposure an individual may realistically experience while performing a label-prescribed activity. In order to estimate this "upper bound" of daily exposure, WHS generally uses the estimated population 95th percentile of daily exposure. When the exposure is estimated from surrogate data, an upper

confidence limit on the percentile is used to account for some of the added uncertainty due to using surrogate data, and to increase the confidence in the estimate. A population estimate is used instead of a sample statistic because sample maxima and upper-end percentiles, in samples of the sizes usually available to exposure assessors, are both statistically unstable and known to underestimate the population values. The population estimate, on the other hand, is more stable because it is based on all the observations rather than a single value; moreover, it is adjusted, in effect, for sample size, correcting some of the underestimation bias due to small samples. A high percentile is estimated, rather than the maximum itself, because in theory, the maximum value of a lognormal population is infinitely large. In practice, exposures must be bounded because a finite amount of active ingredient (AI) is applied. The use of a high percentile acknowledges that the assumed lognormal distribution is probably not a perfect description of the population of exposures, especially at the upper extremes. The population 95th is estimated, rather than a higher percentile, because the higher the percentile the less reliably it can be estimated and the more it tends to overestimate the population value (Chaisson *et al.*, 1999).

For intermediate- and long-term exposure, WHS uses the arithmetic mean of daily exposure to estimate the average. WHS assumes that with increased exposure duration, repeated daily exposure at the upper-bound level is unlikely. When the exposure is estimated from surrogate data, an upper confidence limit on the arithmetic mean is used instead of the mean itself, to account for some of the added uncertainty due to using surrogate data, and to increase the confidence in the estimate. The arithmetic mean is used rather than the geometric mean or the median because, although it can be argued that the latter statistics better indicate the location of the center of a skewed distribution, it is not the center that is of interest in exposure assessment, but the *expected magnitude* of the long-term exposure. While extremely high daily exposures are low-probability events, they do occur, and the arithmetic mean appropriately gives them weight in proportion to their probability. (In contrast, the geometric mean gives decreasing weight as the value of the exposure increases, and the median gives no weight whatsoever to extreme exposures.) In most instances, the mean daily exposure of individuals over time is not known. However, the mean daily exposure of a group of persons observed in a short-term study is believed to be the best available estimate of the mean for an individual over a longer period. The method of approximation is described in Powell (2002). Briefly, the arithmetic mean of total exposure was multiplied by constants that increased as the median number of observations decreased; that is, estimates of the 95th percentile and the 90% confidence limit of ADD were greater in cases where PHED data sets had fewer observations.

To comply with the label requirements and California regulations, groundboom applicators must wear coveralls, gloves, protective eyewear, head coverings and respirators. The mixing/loading process must be conducted using a closed system since the products are Toxicity Category I liquid pesticides (3 CCR, 6746). Aerial application exposure estimates assumed a closed system for mixing/loading and that all handlers (mixer/loaders, applicators and flaggers) wear the clothing and PPE listed on product labels, included long-sleeved shirt and pants, shoes plus socks, chemical resistant gloves, and a respirator. Applicators (pilots) are not required to wear gloves during an application (3 CCR 6738), and were assumed to wear no gloves. Also, pilots do not wear respirators in order to avoid creating a safety hazard.

The identified job categories, PHED exposure estimates and assumptions, and calculations used to calculate the ADDs are given in Tables 3 - 6. Figures 6 - 9 contain the exposure data obtained from PHED.

Scenario of Mixer/Loaders, Closed System, Liquids

Table 3-1. Description of PHED Subset for Scenario of Mixer/Loaders, Closed System, Liquids a

Parameter	Specifications used to generate subset ^a	Actual characteristics of resulting subset
Data Quality Grades b	A,B	A,B
Liquid Type	Emulsifiable concentrate, aqueous suspension, microencapsulated, solution, or undiluted liquid	All emulsifiable concentrate
Mixing Procedure	Closed, mechanical pump or gravity feed	Closed

^a Subset of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.

Figure 6. Summary of Results from the Pesticide Handlers Exposure Database (PHED) Dermal Subset for Scenario of Mixer/Loaders Using Closed System, Copied from the Results Screen Displayed after Inputs for Exposure Calculations have been Entered ^a

Subset Name: S6DERMAL.MLOD

SUMMARY STATISTICS FOR CALCULATED DERMAL EXPOSURES

SCENARIO: Long pants, long sleeves, gloves

PATCH	MICROGRAMS	; PER LB AI MI	XED	
LOCATION	Mean	Coef of Var	Geo. Mean	Obs.
HEAD (ALL)	1.6959	121.3279	.9508	22
NECK.FRONT	1.5225	278.5222	.2418	22
NECK.BACK	.456	280.8991	.0729	22
UPPER ARMS	1.3441	96.6967	.7988	21
CHEST	1.8416	93.4405	1.0577	16
BACK	1.8416	93.4405	1.0577	16
FOREARMS	.5474	98.5203	.3206	21
THIGHS	2.3398	81.9301	1.5773	16
LOWER LEGS	1.292	85.7276	.8778	21
0 0 1			1 1 0	

^a Subset criteria included actual and estimated head patches. Of the 22 head observations, all were actual.

Table 3-2. PHED data from Dermal, Hand, and Inhalation Subsets for Scenario of Mixer/Loaders ^a

Exposure Category	Exposure (µg/lb AI handled)	Adjusted Exposure		Short-Term Multiplier ^c	
Dermal (non-hand) ^d	13.55	10.69	21 e	4	1
Hand	5.72	5.72	31	4	1
Inhalation	0.128	0.128	27	4	1

^a Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).

^b Unless listed separately in this table, data quality for Airborne, Dermal Uncovered, Dermal Covered and Hand are all Grade A or B. Data quality grades are defined in the text and in Versar (1992).

^b Adjusted Exposure data mean PHED data were adjusted by protection factors, including:

Chest and front half of thighs (1/2 of thighs) data multiplied by 0.05 for use of chemical-resistant apron (Thongsinthusak, 1993). Therefore, the dermal (non-hand) exposure (μ g/lb AI handled) is corrected to 13.55 – 1.84 + (1.84 x 0.05) – (2.34 x 1/2) + (2.34 x 1/2 x 0.05) = 10.69

^c Multipliers are explained in text and in Powell (2002).

^d Dermal total includes addition of default feet value of 0.52 x 1.29 (value for lower legs); ratio of feet/lower leg surface area (U.S. EPA, 1997).

^e Median number of replicates used in Dermal (non-hand).

Table 3-3. Values Used in Short-Term and Long-Term Exposure Calculations for Scenario of Mixer/Loader^a

	Short-Term	Long-Term
Total Dermal	$4(10.69) + 4(5.72) = 65.64 \mu\text{g/lb}$ AI handled	$1(10.69) + 1(5.71) = 16.40 \mu g/lb$ AI handled
Inhalation	$4(0.128) = 0.512 \mu\text{g/lb}$ AI handled	$1(0.128) = 0.128 \mu\text{g/lb AI handled}$

a. Values from Table 3-2.

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• Scenario of Aerial Applicator, Liquids, Closed Cockpit

4 5

Table 4-1. Description of PHED Subset for Scenario of Aerial Applicator ^a

Parameter	Specifications used to generate subset ^a	Actual characteristics of resulting subset
Data Quality Grades b	A,B,C	A,B,C
Hands	A,B	A,B
Liquid Type	Not specified	All emulsifiable concentrate
Solid Type	Exclude granular	None
Application Method	Fixed- or rotary-wing	Fixed- or rotary-wing
Cab Type	Closed Cab, closed windows or Closed	Closed Cab, closed windows or Closed
	Cab, closed windows with filtered air	Cab, closed windows with filtered air

^a Subset of Applicator data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.

9 10 11

12

13

6 7

8

Figure 7. Summary of Results from the Pesticide Handlers Exposure Database (PHED) Dermal Subset for Scenario of Aerial Applicator, Copied from the Results Screen Displayed after Inputs for Exposure Calculations have been Entered ^a

SUMMARY STATISTICS FOR CALCULATED DERMAL EXPOSURES

SCENARIO: Long pants, long sleeves, no gloves

PATCH	MI CROGRAMS	PER LB AI SF	RAYED		
LOCATION	Mean	Coef of Var	Geo. Mean	Obs.	
HEAD (ALL)	.4689	190.9362	.2178	28	Subset Name:
NECK.FRONT	.0413	164.4068	.0239	28	
NECK.BACK	.033	181.8182	.0169	28	S18DERMAL.APPL
UPPER ARMS	.3274	44.4411	.3117	16	
CHEST	.355	0	.355	14	
BACK	.355	0	.355	14	
FOREARMS	.1452	35.124	.139	10	
THIGHS	.382	0	.382	14	
LOWER LEGS	.2975	54.6555	.273	16	

^a Subset criteria included actual and estimated head patches. Of the 28 head observations, all were actual.

Table 4-2. PHED data from Dermal, Hand, and Inhalation Subsets for Scenario of Aerial Applicator^a

Exposure Category	Exposure (µg/lb AI handled) ^a	Replicates in subset	Short-Term Multiplier ^b	Long-Term Multiplier ^b
Dermal (non-hand) ^c	2.56	16 ^d	5	1
Hand	9.57	36	4	1
Inhalation	0.025	15	5	1

^a Results from subsets of aerial applicator data in the Pesticide Handlers Exposure Database (PHED).

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^b Data quality for Airborne, Dermal Uncovered and Dermal Covered were all Grade A, B or C. Data quality grades are defined in the text and in Versar (1992).

^b Multipliers are explained in text and in Powell (2002).

^c Dermal total includes addition of default feet value of 0.52 x 0.30 (value for lower legs); ratio of feet/lower leg surface area (U.S. EPA, 1997).

^d Median number of replicates used in Dermal (non-hand).

Table 4-3. Values Used in Short-Term and Long-Term Exposure Calculations for Scenario of Aerial Applicator^a

	Short-Term	Long-Term
Total Dermal	$5(2.56) + 4(9.57) = 51.1 \mu\text{g/lb}$ AI handled	$1(2.56) + 1(9.57) = 12.1 \mu\text{g/lb}$ AI handled
Inhalation	$5(0.025) = 0.125 \mu\text{g/lb AI handled}$	$1(0.025) = 0.025 \mu \text{g/lb AI handled}$

^aValues from Table 4-2.

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• Scenario of Groundboom Applicator, Open Cab:

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Table 5-1. Description of PHED Subset for Scenario of Groundboom Applicator, Open Caba

		Actual characteristics of
Parameter	Specifications used to generate subset ^a	resulting subsets
Data Quality Grades b	A,B	A,B
Liquid Type or Solid Type	Not specified	Emulsifiable concentrate or
		wettable powder
Application Method	Groundboom, Truck or Tractor	Groundboom, Tractor (all)
Cab Type	Open Cab or Closed Cab with Open	Open Cab or Closed Cab with
	Window	Open Window

^a Subset of Applicator data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.

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Figure 8. Summary of results from the Pesticide Handlers Exposure Database (PHED) Dermal Subset for Scenario of Groundboom Applicator, Copied from the Results Screen Displayed after Inputs for Exposure Calculations have been Entered ^a

SUMMARY STATISTICS FOR CALCULATED DERMAL EXPOSURES

SCENARIO: Long pants, long sleeves, no gloves

PATCH LOCATION HEAD (ALL) NECK.FRONT NECK.BACK UPPER ARMS CHEST BACK FOREARMS THIGHS	Mean 2.7891 1.5763 1.0063 1.6914 1.7581 3.0175 2.7301 3.1255	PER LB AI SE Coef of Var 136.1192 167.9503 173.5765 88.749 98.5154 233.2361 419.1055 185.5703	Geo. Mean 1.0464 .3296 .2335 1.1637 1.1329 1.3959 .564 1.1806	0bs. 33 23 29 32 42 42 32 33	Subset Name: S11DERMAL.APPL
THIGHS	3.1255	185.5703	1.1806	33	
LOWER LEGS	2.1148	172.3425	.7466	35	

^a Subset criteria included actual and estimated head patches. Of the 33 head observations, all were actual.

^b Unless listed separately in this table, data quality for Airborne, Dermal Uncovered, Dermal Covered and Hand are all Grade A or B. Data quality grades are defined in the text and in Versar (1992).

Table 5-2. PHED Data from Dermal, Hand, and Inhalation Subsets for Scenario of Groundboom Applicator ^a

Exposure Category	Exposure	Adjusted Exposure	Replicates	Short-Term	Long-Term
	(μg/lb AI handled) ^a	(μg/lb AI handled) ^b	in subset	Multiplier ^c	Multiplier ^c
Dermal (non-hand) ^d	20.91	12.27 ^e	33	4	1
Hand	45.64	4.56	29	4	1
Inhalation	1.18	0.12	22	4	1

^a Results from subsets of groundboom applicator data in the Pesticide Handlers Exposure Database (PHED).

- Chest, back, upper arms, and thighs data multiplied by 0.1 for wear coveralls over a short-sleeve shirt and short pants (Thongsinthusak, 1993). Therefore, the dermal (non-hand) exposure (μg/lb AI handled) is corrected to: 20.91 (1.69+1.76+3.02+3.13) + (1.69+1.76+3.02+3.13) x 0.1 = 12.27.
- Hand data multiplied by 0.1 for use of gloves (Aprea et al., 1994).
- Inhalation data multiplied by 0.1 for use of a half-face respirator with a prefilter (NIOSH, 1987).
- ^c Multipliers are explained in text and in Powell (2002).

Table 5-3. Values Used in Short-Term and Long-Term Exposure Calculations for Scenario of Groundboom Applicator ^a

	Short-Term	Long-Term
Total Dermal	$4(12.27) + 4(4.56) = 67.32 \mu g/lb$ AI handled	$1(12.27) + 1(4.56) = 16.83 \mu g/lb$ AI handled
Inhalation	$4(0.12) = 0.48 \mu \text{g/lb AI handled}$	$1(0.12) = 0.12 \mu \text{g/lb AI handled}$

^aValues from Table 5-2.

• Scenario of Flagger, Liquids

Table 6-1. Description of PHED Subset for Scenario of Flagger, Liquids ^a

	Specifications used	Actual characteristics of resulting
Parameter	to generate subset ^a	subset
Data Quality Grades b	A,B	A,B
Liquid Type or Solid Type	Not specified	Emulsifiable concentrate or dry flowable.
Application Method	Fixed- or rotary-wing	All rotary-wing

^a Subset of Flagger data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.

Figure 9. Summary of Results from the Pesticide Handlers Exposure Database (PHED) Dermal Subset for Scenario of Flagger, Copied from the Results Screen Displayed after Inputs for Exposure Calculations have been Entered ^a

SUMMARY STATISTICS FOR CALCULATED DERMAL EXPOSURES

SCENARIO: Long pants, long sleeves, gloves

PATCH	MICROGRAMS	PER LB AI SP	RAYED		
LOCATION	Mean	Coef of Var	Geo. Mean	Obs.	
HEAD (ALL)	11.3028	127.5702	5.6188	18	Subset Name:
NECK.FRONT	.9533	134.3334	.5146	18	
NECK.BACK	1.4111	215.8529	.4931	18	S7DERMAL.FLAG
UPPER ARMS	3.9285	195.1025	.8284	28	
CHEST	5.1065	188.8378	1.0384	26	
BACK	5.1065	188.8378	1.0384	26	
FOREARMS	1.802	179.5283	.3837	28	
THIGHS	4.0404	308.6996	.9165	26	
LOWER LEGS	2.448	305.6618	.612	28	

^a Subset criteria included actual and estimated head patches. Of the 18 head observations, all were actual.

^b Adjusted Exposure data mean PHED data were adjusted by protection factors, including:

^d Dermal total includes addition of default feet value of 0.52 x 2.11 (value for lower legs); ratio of feet/lower leg surface area (U.S. EPA, 1997).

^e Median number of replicates used in Dermal (non-hand).

^b Unless listed separately in this table, data quality for Airborne, Dermal Uncovered, Dermal Covered and Hand are all Grade A or B. Data quality grades are defined in the text and in Versar (1992).

Table 6-2. PHED data from Dermal, Hand, and Inhalation Subsets for Scenario of Flagger a

	· · · · · · · · · · · · · · · · · · ·					
Exposure Category	Exposure (µg/lb AI handled)	Adjusted Exposure (μg/lb AI handled) ^b	Replicate s in subset	Short-Term Multiplier ^c	Long-Term Multiplier ^c	
Dermal (non-hand) ^d	37.37	26.64	26 ^e	4	1	
Hand	5.97	5.97	30	4	1	
Inhalation	0.20	0.02	28	4	1	

^a Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).

- Head data multiplied by 0.05 for use of headgear based on the assumption that headgear material provides similar protection of chemical-resistant PPE. Therefore, the dermal (non-hand) exposure (μ g/lb AI handled) is corrected to: $37.37 11.3 + (11.3 \times 0.05) = 26.64$.
- Inhalation data multiplied by 0.1 for use of a half-face respirator with a prefilter (NIOSH, 1987).

Table 6-3. Values Used in Short-Term and Long-Term Exposure Calculations ^a

	Short-Term	Long-Term
Total Dermal	$4(26.64) + 4(5.97) = 130.44 \mu g/lb$ AI handled	$1(26.64) + 1(5.97) = 32.61 \mu g/lb$ AI handled
Inhalation	$4(0.02) = 0.08 \mu \text{g/lb AI handled}$	$1(0.004) = 0.004 \mu \text{g/lb AI handled}$

^aValues from Table 8-2.

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16 Table 7 summarizes the estimated absorbed daily dosage for handlers of methamidophos.

^b Adjusted Exposure data mean PHED data were adjusted by protection factors, including:

^c Multipliers are explained in text and in Powell (2002).

^d Dermal total includes addition of default feet value of 0.52 x 2.45 (value for lower legs); ratio of feet/lower leg surface area (U.S. EPA, 1997).

^e Median number of replicates used in Dermal (non-hand).

1 Table 7. Pesticide Handler Exposure Database (PHED) Exposure Estimates for Handlers of Methamidophos.

		Exp	Exposure d		Absorbed Daily Dosage e	
Job	Application	(µg/lb AI handled)		(με	g/kg/day)	
Category a	Method b,c	Dermal	Inhalation	Dermal	Inhalation	Total
M/L	Aerial (350 A/day)	16.41	0.128	23.90	0.643	24.54
	Aerial (1200 A/day)	16.41	0.128	81.93	2.204	84.14
	Groundboom (80 A/day)	16.41	0.128	5.46	0.147	5.61
	Groundboom (200 A/day)	16.41	0.128	13.66	0.367	14.02
	Chemigation (350 A/day)	16.41	0.128	23.90	0.643	24.54
Applicator	Aerial (350 A/day)	12.13	0.025	17.66	0.126	17.79
	Aerial (1200 A/day)	12.13	0.025	60.56	0.430	60.99
	Groundboom (80 A/day)	16.83	0.12	5.60	0.138	5.74
	Groundboom (200 A/day)	16.83	0.12	14.00	0.344	14.35
M/L/A f	Groundboom (70 A/day)	16.79	0.121	4.89	0.121	5.01
	Groundboom (180 A/day)	16.79	0.121	12.57	0.312	12.88
Flagger	Aerial (350 A/day)	32.61	0.02	47.49	0.100	47.59
	Aerial (1200 A/day)	32.61	0.02	162.82	0.344	163.16

- a Protective clothing and equipment for various scenarios based on product label and regulation:
 - Mixer/loader (M/L) and mixer/loader/applicator (M/L/A) use a closed system to mix or load, according to California regulations (3 CCR 6746[a]), and were assumed to substitute coveralls, chemical-resistant gloves, and a chemical resistant apron for PPE required by the product labeling (3 CCR 6738[i]), protective eyewear is required (3 CCR 6738[b]), shoes plus socks are assumed to be worn.
 - Flagger additionally wears headgear based on product label.
 - Pilot used a closed cockpit aircraft (U.S. EPA, 1999a). Pilots were assumed to wear long-sleeved shirt and pants, shoes plus socks. Applicators (pilots) are not required to wear gloves during an application (3 CCR 6738), and do not wear respirators avoiding safety hazard.
- b Daily treated acres in each scenario were dependent on the estimates of U.S. EPA (2002):
 - 200 acres (A) groundboom application on cotton; 80 acres for groundboom application on potato/tomato;
 - 1200 acres for aerial application on cotton; 350 acres for chemigation and aerial application on potato/tomato.
 - 180 acres for groundboom mixer/loader/applicator for cotton; 70 acres for groundboom mixer/loader/applicator for potato/tomato. This estimate assumes that mixing/loading accounts for 10% of the work time, and application accounts 90% of the work time of a mixer/loader/applicator (Brodberg and Thongsinthusak., 1995).
- c Application rate = 1.0 lb active ingredient (AI)/acre.
- d From PHED software (U.S. EPA, 1998). Dermal data represents sum of dermal (non-hand) and hand. Appropriate protection factors were applied as explained in the text and listed in Tables 3-6.
- e Absorbed Daily Dosage = Exposure x absorption rate x application rate x acres/day ÷ body weight. Calculation assumptions include:
 - The maximum label rate of 1.0 lb AI/acre was used for all scenarios;
 - Dermal absorption rate = 29% (Thongsinthusak, 2001c);
 - Inhalation uptake = 100%;

- Body weight = 69.7 kg for both male and female (U.S. EPA, 1997).
- f M/L/A: mixer/loader/applicator. Since there is no available scenario for groundboom M/L/A with closed mixing system and open cab in PHED, the exposures of M/L/A of groundboom were estimated by combining the exposures of mixer/loader of groundboom and exposures of applicator of groundboom. It is assumed that mixing/loading accounts for 10% of workday, and application accounts for 90% of workday (Brodberg and Thongsinthusak, 1995).

As mentioned above, to estimate intermediate- and longer-term exposures, WHS used the average daily exposure. Over these periods of time, a worker is expected to encounter a range of daily exposures. The temporal patterns for the handlers were investigated by plotting percent of annual use based on numbers of applications per month for 1998 - 2002 (DPR, 2004). The data from all counties of California with methamidophos applications on cotton, potatoes and

tomatoes were summarized in Figure 10. To estimate annual exposure, months in which >5% of the annual applications occurred were counted as part of the typical application season. The 5% default is an arbitrary cutoff based on the assumption that workers are more likely to be exposed during months with high use. Most use of methamidophos (>85%) occurs in 4 months, June through September.

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Figure 10. Applications of Methamidophos to Cotton, Potatoes and Tomatoes in California, 1998 - 2002.

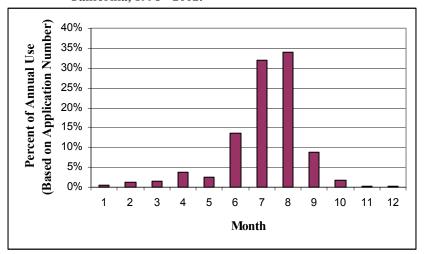


 Table 8 summarizes the estimates of acute, seasonal, annual, and lifetime exposures for methamidophos handlers.

Table 8. Estimates of Pesticide Handler Exposure to Methamidophos.

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2	Job	Annual Use	Acute ADD d	SADD ^e	AADD ^f	LADD ^g	
3	Category a,b	(# Months) ^c	(µg/kg/day)	(µg/kg/day)	(µg/kg/day)	(µg/kg/day)	
4	Mixer/Loader						
5	Aerial (350 A/day)	4	98.2	24.54	8.18	4.36	
6	Aerial (1200 A/day)) 4	336.5	84.14	28.05	14.96	
7	Chemigation (350 A	A/day) 4	98.2	24.54	8.18	4.36	
8	Groundboom (80 A	/day) 4	22.4	5.61	1.87	1.00	
9	Groundboom (200 A	4/day) 4	56.1	14.02	4.67	2.49	
10	<u>Applicator</u>						
11	Aerial (350 A/day)	4	75.0	17.79	5.93	3.16	
12	Aerial (1200 A/day)) 4	257.2	60.99	20.33	10.84	
13	Groundboom (80 A	/day) 4	23.0	5.74	1.91	1.02	
14	Groundboom (200 A	4/day) 4	57.4	14.35	4.78	2.55	
15	M/L/A						
16	Groundboom (70 A	/day) 4	20.0	5.01	1.67	0.89	
17	Groundboom (180 A	4/day) 4	51.5	12.88	4.29	2.29	
18	<u>Flagger</u>						
19	Aerial (350 A/day)	4	190.4	47.59	15.86	8.46	
20	Aerial (1200 A/day)) 4	652.6	163.16	54.39	29.01	

a M/L/A: mixer/loader/applicator.

- b Daily treated acres in each scenario were dependent on the estimates of U.S. EPA (2002):
 - 200 acres (A) groundboom spray application on cotton; 80 acres for groundboom spray application on potato/tomato;
 - 1200 acres for chemigation and aerial application on cotton; 350 acres for chemigation and aerial application on potato/tomato.
 - 180 acres for groundboom mixer/loader/applicator for cotton; 70 acres for groundboom mixer/loader/applicator for potato/tomato. The estimate based on that mixing/loading account for 10% of work time, and application account 90% of work time of a mixer/loader/applicator (Brodberg and Thongsinthusak., 1995).
- c The estimated use season for handlers was based on California Pesticide Use Summaries Database (DPR, 2004, see Figure 10).
- d Acute Absorbed Daily Dosage (Acute ADD) is an upper confidence limit on the 95th percentile estimate of data from the PHED (see discussion under Exposure of Handlers); Multipliers from Powell (2002).
- e Seasonal Average Daily Dosage (SADD) is a 90% confidence limit estimate of the average daily absorbed dose (see discussion under Exposure of Handlers); Multipliers from Powell (2002).
- f Annual Average Daily Dosage (AADD) = SADD x # months used per year/12 months in a year.
- g Lifetime Annual Daily Dosage (LADD) = AADD x 40 years of work in a lifetime/75 years in a lifetime.

2. Exposure of Fieldworkers

Harvesters and other fieldworkers are subject to occupational exposure to methamidophos from contact with dislodgeable foliar residues on treated foliage. Chemical-specific data for reentry exposure to methamidophos are not available. For these fieldworkers, it is thus necessary to extrapolate dermal exposure from available DFR data and a dermal transfer factor (TF). TF is defined as the ratio of hourly dermal exposure in µg/hr to DFR in µg/cm². When multiplied by a proper dermal transfer factor, the DFR may be converted to hourly dermal exposure of workers entering a treated field. Transfer factors and DFR values are used to estimate potential human exposure of fieldworkers performing different activities (e.g., scouting, harvesting, pruning, etc.). Reentry workers are not required to wear protective clothing unless entering before expiration of the REI. Therefore, fieldworker exposure calculations were not corrected for any

protection factor. For all crops, the maximum application rate is 1.0 lbs AI/acre, and the REI is 3 days.

In the absence of adequate exposure data for workers entering treated fields, residue decay data and transfer factors (based on standards by U.S. EPA Science Advisory Council for Exposure, US. EPA, 2000b) were used to estimate worker exposure. Short-term exposures were estimated at the expiration of the REI for all activities except hand harvesting of tomatoes and potatoes, which were estimated at the expiration of the PHIs (Table 9). For intermediate- and long-term exposure estimates, it was assumed that workers would enter fields at an average time somewhat after the expiration of the REI or PHI, based on how frequently specific activities occur in general crop types (UCCE, 2002). Intermediate- and long-term exposures were estimated at an assumed average reentry of REI + 7 days (postapplication Day 7) for scouting in cotton, scouting and irrigating in tomatoes, staking/tying in tomatoes, and transplanting tomatoes. Intermediate- and long-term exposures were estimated at an assumed average reentry of PHI + 7 days for workers hand harvesting tomatoes (postapplication Day 14) and hand harvesting potatoes (postapplication Day 21). The annual exposure period is estimated based on the application data (UCD, 2002) as shown in Figures 11-12 and farm worker activity data (Edmiston *et al.*, 1997) as shown in Table 10.

Studies of reentry worker exposure in crops treated with organophosphates (Ware *et al.*, 1973, 1974, 1975) suggest that inhalation is a relatively minor exposure route. U.S. EPA also anticipated that inhalation exposure would be negligible in reentry workers (U.S. EPA, 1999a). Only dermal exposure was considered for fieldworkers.

Cotton scouting

Cotton scouts are subject to occupational exposure from contact with dislodgeable methamidophos residues that have accumulated on treated foliage. The REI is 3 days in California. The DFR was estimated based on the study done in cotton in California (Fujie, 1986), as discussed in the DFR section. TF are residues transferred to skin, the values are taken from Agricultural Default Transfer Coefficients (U.S. EPA, 2000b). The default workday was assumed 6 hours (Dong, 1994). The acute ADD for cotton scouts was estimated as shown in Table 9.

Seasonal and annual exposures were estimated based on the high-use periods of methamidophos on cotton. Figure 11 shows the relative numbers of applications to cotton on a monthly basis for the most recent five years, 1998-2002 (DPR, 2004). High-use periods (> 5% of annual use) occurred in a three-month interval, June through August. For seasonal and annual exposure estimates, it was assumed that scouts were exposed on each workday for the three months that account for 92% of annual applications. The estimated SADD, AADD, and LADD were summarized in Table 11.

Table 9. Estimated Dermal Exposure of Fieldworkers to Methamidophos.

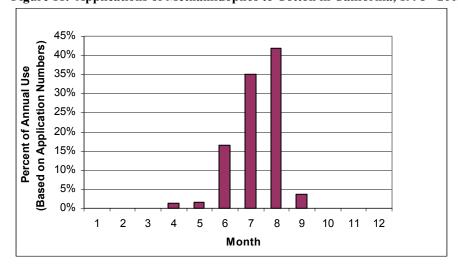
2 3	Job Category ^a	REI/PHI ^b (day)	DFR ^c (µg/cm ²)	TF ^d (cm ² /hr)	Daily Exposure ^e (μg/person/day)	
4	Cotton					_
5	Scout	3	0.094	1,500	846	3.52
6	<u>Tomatoes</u> ^g					
7	Scout, irrigate	3	0.133	700	745	3.10
8	Stake, tie	3	0.133	1,000	1064	4.43
9	Transplant, prune	3	0.133	1,000	1064	4.43
10	Harvest	7	0.053	1,000	424	1.76
11	<u>Potatoes</u>					
12	Harvest (by hand)	14	0.025	1,000	200	0.83

- Workers were assumed to wear long pants, a long-sleeved shirt, and no gloves.
- PHI (pre-harvest interval) were dependent on product labels. REI (restricted entry interval) was determined to be 3 days based on California regulations (3 CCR 6774(e)) and the product label.
- DFR (dislodgeable foliar residues) values at the REI or PHI, see Dislodgeable Foliar Residues section.
 - TF (transfer factor) are residues transferred to skin. The values are taken from Agricultural Default Transfer Coefficients (U.S. EPA, 2000b).
 - Daily exposure (μ g/person/day) = DFR at the expiration of the REI/PHI x TF x work hours/day (For cotton scouting, the work hour was 6 hours/day based on Dong, 1994; and for other job categories, the default work hours were 8 hr/day based on U.S. EPA, 1999a).
 - Acute Absorbed Daily Dosage (Acute ADD) = DFR at the expiration of the REI/PHI x TF x work hours/day x 29% dermal absorption (Thongsinthusak, et al., 1993) ÷ 69.7 kg body weight (U.S. EPA, 1997).
 - DFR values were based on a study conducted in Fresno, CA (U.S. EPA, 1999a).

Cotton harvesting

Since cotton is harvested mechanically and the PHI for cotton is 50 days, cotton harvester exposure to methamidophos is assumed to be minimal.

Figure 11. Applications of Methamidophos to Cotton in California, 1998 - 2002.



Tomato scouting and irrigating

Exposure data for workers entering treated tomato fields is not available. Residue decay data and transfer factors were used to estimate worker exposure at the expiration of the REI. The default work hours per day for tomato scouting and irrigating were assumed 8 hours (U.S. EPA, 1999a). The acute ADD for tomato scouting and irrigating was estimated as shown in Table 9.

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Seasonal and annual exposures were estimated based on the high-use periods of methamidophos on tomatoes. Figure 12 shows the relative numbers of applications to tomatoes on a monthly basis for the most recent four years for which data are available, 1998 - 2002 (DPR, 2004). High-use periods (> 5% of annual use) occurred in a 4-month interval, June through September. For seasonal and annual exposure estimates, it was assumed that scouts were exposed on each workday for the four months that account for 84% of annual applications. The estimated SADD, AADD, and LADD were summarized in Table 11.

Tomato staking and tying

The acute ADD for a tomato staker and tier was estimated as shown in Table 9, based on DFR and TF mentioned above. The default work hours per day for tomato staking and tying were assumed 8 hours (U.S. EPA, 1999a). For seasonal and annual exposure, the peak activity periods occur in early April to late April, and the total activity periods occur in March to May (Table 10) based on the farm worker activity data (Edmiston *et al.*, 1997). Based on the PUR data, monthly applications did not exceed 5% of annual applications during these three months. However, there are still some applications during these months (1.7%, 3.3%, and 3.5% in March, April and May, respectively). Therefore, the annual exposure to methamidophos by workers involved in tomato staking and tying is assumed to occur in one month. The SADD and AADD were estimated as shown in Table 7.

Figure 12. Applications of Methamidophos to Tomatoes in California, 1998 - 2002.

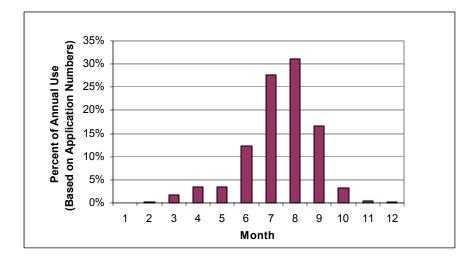


Table 10. Reported Reentry Activities Periods for Fieldworkers on Tomatoes. ^a

Crop	Activities	Location	Peak Activity Period	Total Activity Period
Tomatoes	Stake, tie	Tulare	early Apr – late Apr	late Mar – early May
	Transplant, prune	Merced	Apr – May	Feb – early June
	Harvest	Fresno	June – Aug	May - Nov
		Kern	July – July	June – Aug
		Kings	July – Aug	May – Sept
		Merced	June – July	June – Nov
		San Joaquin	Aug – Sept	July – Nov
		Stanislaus	Aug – Oct	July – Nov
		Tulare	June – July	June – Aug

^a Data from California Farm Worker Activity Profile database (Edmiston *et al.*, 1997).

Tomato transplanting and pruning

The acute ADD for tomato transplanting and pruning was estimated as shown in Table 9, based on DFR and TF mentioned above. The default work hours per day for tomato transplanting and pruning were assumed 8 hours (U.S. EPA, 1999a). For seasonal and annual exposure, the peak activity periods occur from April to May, and total activity period occur from February to June (Edmiston *et al.*, 1997) as shown in Table 10. The data from PUR indicate that the high-use periods (>5% of annual use) occurred from June through September. Based on these data, the annual exposure period to methamidophos by workers involved in tomato transplanting and pruning is assumed to be 1 month, June. The period of February to May is not included since few applications (< 5% of annual application) occur in these months. The SADD and AADD were estimated as shown in Table 11.

Tomato harvesting

Although tomatoes for processing are harvested by machines, fresh market tomatoes are still harvested by hand. The PHI for tomatoes is 7 days (see Reentry Interval/Preharvest Interval section). The acute ADD for tomato harvesting was estimated as shown in Table 9, based on DFR and the TF mentioned above. The default work hours per day for tomato harvesting were assumed 8 hours (U.S. EPA, 1999a). For seasonal and annual exposure, the peak activity periods occur from June through October, and total activity periods occur from May through November (Edmiston *et al.*, 1997) as shown in Table 6. Data from the PUR indicate that the high-use periods (>5% of annual use) occurred from June through September. Based on these data, the annual exposure to methamidophos by workers involved in tomato harvesting is estimated to occur in 4 months, June to September. May, October, and November are not included since few applications (< 5% of annual application) occur in these months. The estimated SADD, AADD, and LADD are summarized in Table 11.

Potato harvesting

Potatoes are almost entirely mechanically harvested in California. Less than 5% of the potato crop is harvested by hand, and 3-4 days are needed (the information was provided by staff at Siskiyou County, a leading county in potato production). The PHI for potatoes is 14 days. The acute ADD for potato harvesting was estimated as shown in Table 9. The default work hours per

day for potato harvesting were assumed 8 hours (U.S. EPA, 1999a). The SADD, AADD, and LADD were considered insignificant because of the short-term exposure.

Table 11. Estimates of Reentry Workers' Exposure to Methamidophos.

Task	Acute ADD ^a (μg/kg/day)	Average DFR ^b	SADD ^c (µg/kg/day)	Annual Exposure Months d	AADD ^e (μg/kg/day)	LADD ^f (µg/kg/day)
Cotton						
Scout	3.52	0.007	0.26	3	0.07	0.03
<u>Tomatoes</u>						
Scout, irrigate	3.10	0.027	0.63	4	0.21	0.11
Stake, tie	4.43	0.027	0.89	1	0.07	0.04
Transplant, prune	4.43	0.027	0.89	1	0.07	0.04
Harvest	1.76	0.011	0.36	4	0.12	0.06
Potatoes g						
Harvest	0.83	-	-	-	-	-

- 5 a Acute Absorbed Daily Dosage (Acute ADD) is from Table 5.
 - b The average DFRs (dislodgeable foliar residues) are DFR values of seventh day after REI (restricted entry interval) or seventh day after PHI (pre-harvest interval) (see text).
 - c Seasonal Average Daily Dosage (SADD) = Average DFR x dermal transfer factor x work hours/day x dermal absorption (29%) ÷ body weight (69.7 kg). For cotton scouting, the work hour was 6 hours/day based on Dong (1994); and for other job category, the work hours were 8 hr/day based on U.S. EPA (1999a).
 - d The annual exposure months for fieldworkers are determined by comparing the data of total activities periods (Table 6) and application periods (Figure 11 and 12), see text.
 - e Annual Average Daily Dosage (AADD) = SADD x annual exposure months per year \div 12 months in a year.
 - f Lifetime Annual Daily Dosage (LADD) = AADD x (40 years of work in a lifetime) ÷ (75 years in a lifetime).
 - g SADD, AADD and LADD for potatoes harvester are not calculated since exposure is short, see text.

VII. EXPOSURE APPRAISAL

The ideal exposure assessment should be conducted with adequate high quality data. Unfortunately, such data are not available for methamidophos. In the absence of adequate data and information, assumptions are made in the exposure assessment. However, uncertainties are associated with these assumptions. An exposure assessor should openly and honestly discuss the sources of these uncertainties so that the risk manager can put them into perspective. The main uncertainties in this exposure assessment document are listed below.

1. Estimating dermal exposures dependent on PHED data.

In the absence of chemical-specific handler exposure data for methamidophos, we relied on PHED (1995) as surrogate. PHED is not chemical-specific. It uses multiple studies to derive the exposure estimates. In PHED, the reliability is positively related to the number of observations (replications) and the study quality (grade). The limitations of PHED prevent its use for distributional statistics on the exposure estimates. Moreover, since PHED incorporates exposure data from various studies, the minimum detection levels for the analytical method used to detect residues may be different. Therefore, the detection of dermal exposure from the various body regions is not standardized.

Data in PHED are graded, that grading is an indicator of data quality of the studies in the database. These grades are based on Quality Assurance/Quality Control data provided as part of the exposure studies. Grades A and B indicate high-quality studies, with lab recoveries of 90-110% and 80-100%, respectively (field recoveries range 70-120% and 50-120%). Grade C indicate moderate data quality, with lab and field recoveries of 70-120% and 30-120%, respectively. Grade D and E are the lowest quality grade, and are assigned to PHED data that do not meet basic quality assurance (U.S. EPA, 1998). Fifteen or more observations were considered as a sufficient number of records, for use in exposure calculations (U.S. EPA, 1987).

In this document, PHED was used to estimate seven dermal and inhalation exposure scenarios. These exposure values were used to calculate ADDs. Table 12 summarizes the data quality grades and the number of observations contained in each PHED data set used for developing these exposure scenarios.

Table 12. Data Quality in Pesticide Handler Exposure Database (PHED) Used for Developing Handler Exposure Assessment.

Job	Application	Dermal Exposure		Hands Exposure		Inhalation Exposure	
Category	Method	Observations	Grade	Observations	Grade	Observations	Grade
Mixer/Loader	Aerial	16-22	AB	31	AB	27	AB
Mixer/Loader	Chemigation	16-22	AB	31	AB	27	AB
Mixer/Loader	Groundboom	16-22	AB	31	AB	27	AB
Applicator (Pilot)	Aerial	10-28	ABC	36	AB	15	ABC
Applicator	Groundboom	23-42	AB	29	AB	22	AB
Flagger	Aerial	18-28	AB	30	AB	28	AB

The examination of Table 12 reveals that body dermal data quality and hands data quality were high in the subsets used to generate exposure estimates for mixer/loaders, groundboom applicators and aerial flaggers. The number of observations was greater than 15 and the data quality was high. The exposure assessments for these scenarios are reported with high confidence. The body dermal (non-hand) subsets used to generate exposure estimates for aerial applicators with moderate data quality and the number of observations ranging from 10 - 28. The exposure assessments for this scenario are reported with medium confidence. However, the hand data quality was high, and the number of observations greater than 15. The exposure assessments for hand exposure of this scenario are reported with high confidence.

The inhalation data quality was high for mixer/loaders, groundboom applicators, and flaggers, with greater than 15 observations. The exposure assessments for these scenarios are reported with high confidence. Inhalation data quality was moderate for aerial applicators, although with 15 observations. The exposure assessment for this is reported with medium confidence.

U.S. EPA also uses PHED to estimate handler exposure; however, U.S. EPA approaches PHED data somewhat differently than DPR. First, as explained in U.S. EPA's policy for use of PHED data (U.S. EPA, 1999): "Once the data for a given exposure scenario have been selected, the data are normalized (i.e., divided by) by the amount of pesticide handled resulting in standard unit exposures (milligrams of exposure per pound of active ingredient handled). Following normalization, the data are statistically summarized. The distribution of exposure values for each body part (i.e., chest upper arm) is categorized as normal, lognormal, or "other" (i.e., neither

normal nor lognormal). A central tendency value is then selected from the distribution of the exposure values for each body part. These values are the arithmetic mean for normal distributions, the geometric mean for lognormal distributions, and the median for all "other" distributions. Once selected, the central tendency values for each body part are composited into a "best fit" exposure value representing the entire body." In other words, U.S. EPA uses various central tendency estimates (often the geometric mean or median, as PHED data rarely follow a normal distribution), while DPR believes the arithmetic mean is the appropriate statistic regardless of the sample distribution (Powell, 2003). Second, for acute exposure estimates DPR uses a 95th percentile upper bound estimate, while U.S. EPA uses a central tendency estimate for all exposure durations. Third, as explained in the Exposure Assessment section, DPR calculates upper 90% confidence limits for both upper bound and mean exposures, while U.S. EPA does not (note: DPR's policies for handling PHED data have been reviewed informally and are currently under formal review by a statistician at the University of California). The differences between exposure rate and acute exposure estimates calculated according to DPR and U.S. EPA policies are summarized in Table 13 for an example scenario, groundboom mixer/loader. U.S. EPA values are from the RED document (U.S. EPA, 1999a). There is no monitoring study available for comparison.

In Table 13, the exposure rate estimated according to DPR policy is 16.5 µg AI/lb handled. The exposure rate estimated according to U.S. EPA policies is 8.7 µg AI/lb handled. The acute ADD estimated according to DPR policy is 22.4 µg/kg/day. The estimate calculated according to US EPA policy is 9.9 µg/kg/day. Above calculation based on that 80 acres are treated per day for "typical" potato and tomato agricultural groundboom applications (U.S. EPA, 2002a). As analyzed previously, the main reason for the difference between the PHED values from the U.S. EPA and DPR is mean values selected. The U.S. EPA used geometric mean, while DPR used arithmetic mean (Powell, 2003). For acute exposure estimate, DPR calculates upper 90% confidence limits for upper bound (95th percentile) estimate, while U.S. EPA just uses a central tendency estimate.

Table 13. Comparison of Groundboom Mixer/Loader (Closed System) Exposure to Methamidophos Estimated from Surrogate Data by DPR and U.S. EPA Policy

	Exposure rate	Acute ADD
Exposure estimate	(μg AI/lb handled) ^a	(µg/kg/day) ^b
From PHED, according to DPR policy ^c	16.5	22.4
From PHED, according to U.S. EPA (1999a) ^d	8.7	9.9

^a Total exposure rate, dermal, hands plus inhalation.

Acute Absorbed Daily Dosage (ADD) estimates assumed a maximum application rate of 1 lbs AI/acre, and an 8-hour workday. Amount treated was assumed to be 80 acres treated/day (U.S. EPA, 2002) for potato and tomato fields. Dermal absorption assumed to be 29% (Thongsinthusak, 2001c) for DPR estimates, and 100% for U.S. EPA estimates (1999a). Inhalation absorption assumed to be 100% for both DPR and U.S. EPA estimates, and body weight assumed to be 67.9 kg (U.S. EPA, 1997) for DPR estimates, and 70 kg for U.S. EPA estimates (1999a).

^c Department of Pesticide Regulation (DPR) policy described in Exposure Assessment section. Exposure rate and acute ADD are from Table 7 and 8.

^d U.S. Environmental Protection Agency (U.S. EPA) exposure estimates are obtained from U.S. EPA (1999a, Table 9 and 12).

2. Estimating absorbed daily dose using default body weight.

In calculating the absorbed daily dosage in this methamidophos exposure assessment, the average body weight assumed for handlers and fieldworkers was 69.7 kg (male and female) (U.S. EPA, 1997). The exposure rates calculated from PHED were based on the exposure monitoring studies in which the volunteers were primarily male workers. The average body weight for male adults is approximately 10% higher than the average of 69.7 kg assumed here (U.S. EPA, 1997; Thongsinthusak *et al.*, 1993). The use of this default value might have slightly overestimated the dosage of methamidophos for these workers whose exposure rates were calculated from PHED.

3. Estimating seasonal/annual exposure frequencies of handlers and fieldworkers based on Pesticide Use Report (PUR).

PUR data were used to estimate likely periods of worker exposure based on the distribution of applications in California. The seasonal and annual exposure frequencies (4 months) that were assumed for all handlers may be overestimated. It is unlikely that the same worker will apply methamidophos every day in the entire 4-month use period. Since it is hard to know the number of applicators, this conservative estimation was used. Such uncertainty would lead to an overestimation of the annual exposure of methamidophos for these handlers. It is equally unlikely that a fieldworker will work in a methamidophos-treated field every day for 3-4 months.

4. Estimating fieldworker exposure based on DFR data.

For fieldworker exposure, the estimates derived from DFR served as the starting point. Since the DFR values are point estimates, it is not possible to derive the upper bound values for the exposures of fieldworkers. In this assessment document, DFR on the first day after the REI expired was used as the upper bound to estimate acute ADD, which may be an overestimation.

Additionally, for seasonal exposure of fieldworkers, this assessment uses an assumed average reentry date, i.e., DFR values on the REI plus 7 days, or DFR values on the PHI plus 7 days to calculate SADD. These assumed averages were not based on data; rather, they were based on the reasonable assumption that worker may enter fields an average of 7 days after expiration of the REI/PHI. That may not be an accurate estimate of exposure since harvesting and other reentry activities usually occur over a relatively long period (Table 10).

5. There are no SADD, AADD, and LADD estimate for potato harvesters.

As mentioned previously, most potatoes in California are harvested mechanically. For those small farms where potatoes are still harvested by hand, only 3 - 4 days are needed for harvesting (based on the information provided by staff from the leading potato production county, Siskiyou County). A 3- to 4-day exposure is not considered long-term exposure, therefore, SADD, AADD and LADD are not addressed in this document.

6. Cancellation use on cotton.

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In the IRED published by USEPA at the end of 2002, it was stated that the uses of methamidophos on cotton would be cancelled by 2007 due to the ecological toxicity concerns. The cancellation of methamidophos products on cotton should reduce handlers' and scouts' exposure. However, in the next several years, methamidophos still may be used on cotton. Therefore, the exposure for handlers and scouts' in cotton field was assessed in this document.

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7. DPR and U.S. EPA estimates.

The handler exposure estimates described in this exposure assessment document are different from the estimates performed by U.S. EPA (1999a). The sources of these differences include:

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1) U.S. EPA used geometric means to summarize PHED data, whereas DPR used arithmetic means, in according to the usual practice of DPR. Also, U.S. EPA estimates were based on means rather than the upper confidence limits used by DPR. That caused the estimations by DPR to be greater than the estimations by U.S. EPA.

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2) DPR and U.S. EPA might have used different PHED subsets, such as study grades, formulation type selection, mixing and application procedures selection, airborne conditions etc. that may lead to different results.

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